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Optical Fluorescence Analysis of Beryllium Wipes Contaminated with High Levels of Plutonium

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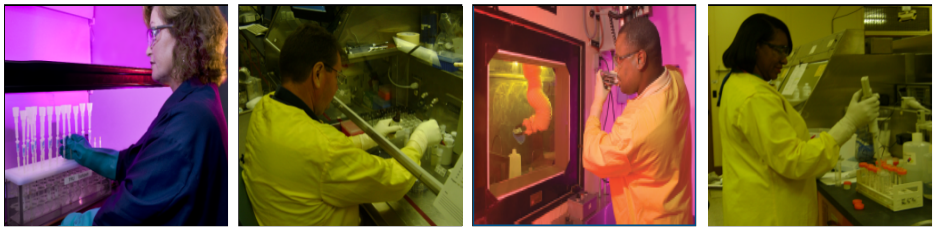
10:35AM



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Summary

- Introduction
- Fluorometer Glovebox Installation
- Method Testing
- Demonstration of Competency
- Interference Testing and Results (Ce and Pu)
- Conclusion
- Acknowledgements

Introduction

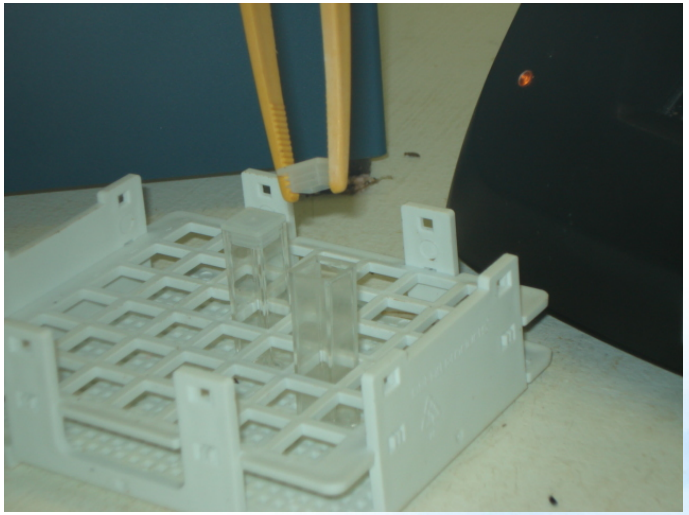
- **Savannah River Site (SRS) radiological IH lab tasked to provide AIHA accredited Be results for GhostWipes™ contaminated with high amounts of plutonium (Pu)**
- **Up to 0.5 gram of Pu/wipe (samples from Pu processing glovebox)**
  - Customer assurance of <0.5 gram of Pu/wipe
- **Routine ICP-AES wipe samples undergo ion exchange (TEVA and Diphonix) for interference removal**
  - Modified NIOSH 7303 ICP, EPA 6010D
  - Glovebox modified ICP-AES is cost prohibitive, long lead time
- **Optical fluorometer and hotblock glovebox installation**
  - Existing method setup in radiohood
  - Comparable to ICP-MS sensitivity
  - More practical, cost effective, and less time to establish compared to a glovebox modified ICP-AES

Glovebox Fluorometer Installation

- **Introduce equipment into glovebox**
  - Fluorometer, hotblock, analytical balance, pipettes, thermometer, and associated cables (USB and power)
    - In-house addition of Amphenol connectors to USB cable for glovebox interfacing
  - Promega GloMax Multi Jr. fluorometer (FI-B) equipped with optical kit FM-B obtained from Berylliant

Glovebox Fluorometer Installation, continued

- **Remotely connect fluorometer console to PC**
- **Establish communication between PC and fluorometer**
- **Method development**
- **Resolve glovebox related, ergonomic issues**
  - Minimize unnecessary glovebox work, prepare as much as possible on benchtop
  - Utilize a click-pen with ink removed as stylus for fluorometer touchscreen
    - Readily available stylus' were too small for glovebox gloves.
  - Utilize long, plastic forceps for handling and manipulating cuvette caps



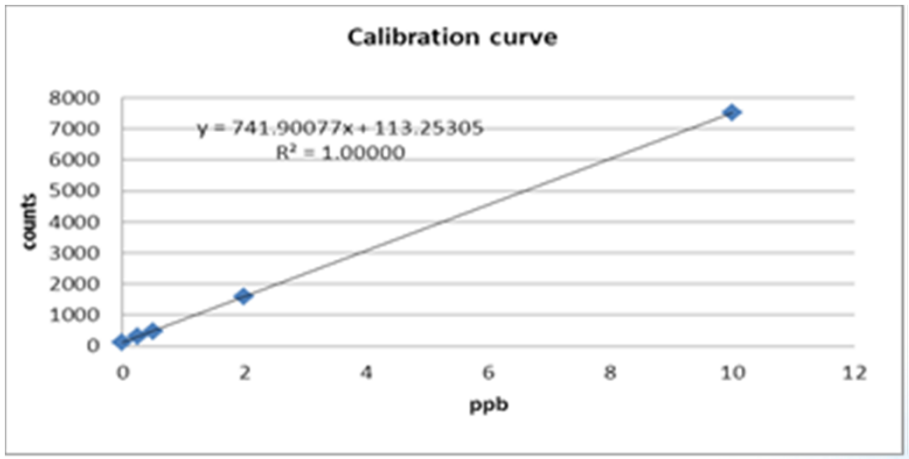
NIOSH 9110 and Other References

- **NIOSH 9110 – Beryllium in Surface Wipes by Field-portable Fluorometry**
  - Alternative to NIOSH 7300 (hotblock digestion and ICP-AES analysis)
- **Purpose: accurately measure beryllium using a basic solution to remove metal contaminants and a dye specific to the beryllium atom.**
  - Hydroxybenzoquinoline sulfonate (HBQS) specific to beryllium
  - Ethylenediaminetetraacetic acid (EDTA) and high alkalinity remove interferences. e.g., Fe and Ti
- **DOE action limit 0.2 µg/100 cm^2**
- **Implement as much as possible from existing publications and SRS radiohood experience**
  - Ashley, K.; Agrawal, A.; Cronin, J.; Tonazzi, J.; McClesky, T. M.; Burrell, A. K.; Ehler, D. S. Ultra-trace determination of beryllium in occupational hygiene samples by ammonium bifluoride extraction and fluorescence detection using hydroxybenzoquinoline sulfonate. **Analytica Chimica Acta** 584. 2007, 281-286.
  - ASTM D7202 - Standard Test Method for Determination of Beryllium in the Workplace Using Field-Based Extraction and Fluorescence Detection

Method Testing

- **Interference testing conducted with and without blank sampling media (GhostWipe™)**
- **3 wt% ammonium bifluoride (ABF) selected for glovebox wipes**
  - Assured dissolution of refractory BeO in highly soiled wipe samples
  - 1 wt% ABF routinely used for wipes and filters in the radiohood
- **Establish working calibration prepared in 3 wt% ABF**
  - 0.00. 0.25, 0.50, 2.0, and 10.0 ppb at instrument
  - Linear calibration range: $R^2 \geq 0.998$
- **BeO CRM filter extractions in 3 wt% ABF**
  - Obtained from High Purity Standards
  - Prepared from NIST SRM 1877 (high-fired BeO powder)

Calibration Data	
Standard Concentration (ppb)	Instrument Counts
0.00	108.80
0.25	307.20
0.50	485.80
2.00	1590.40
10.00	7533.30



Method Testing, continued

- **Wipes submerged in 20 mL of 3 wt% ABF**
- **Heated at 85-90°C for 1 hour**
- **Extractions allowed to cool and settle overnight**
  - Care was taken not to disturb extracted solutions during cooling and aliquoting
- **1 mL of extract was filtered through a 0.2 micron filter**
- **100 µL of filtered extract was added to 1.9 mL of detection solution**
  - Aliquots were taken near the surface of solution
  - Total 400x dilution (20x extraction + 20x detection)
- **Preparations were placed in darkness ~2 hours**
- **Solutions were measured by fluorometry**
  - pH confirmed >12

Demonstration of Competency

- **Demonstration of Competency (DoC) tests are performed in-house in place of Proficiency Analytical Test Samples (PATS)**
  - AIHA BePATS are analyzed by ICP-AES
  - DoC consists of CRM filters blind to the analyst
- **Six BeO CRM filters extracted in 3 wt% ABF**
  - Three 0.2 µg BeO/filter CRMs
  - Three 0.5 µg BeO/filter CRMs
- **Average BeO recovery = 92%**
  - AIHA acceptable recovery range 75 – 125%

	Reference (µg/filter)	Measured (µg/filter)	% recovery
BeO 0.2	0.2	0.172	86.0%
BeO 0.2	0.2	0.192	96.0%
BeO 0.2	0.2	0.160	80.0%
BeO 0.5	0.5	0.472	94.4%
BeO 0.5	0.5	0.520	104.0%
BeO 0.5	0.5	0.460	92.0%

Plutonium and Optical Fluorescence

- **Limited data available describing the effect of Pu on Be by fluorometry**
  - Fluoride necessary to ensure complete dissolution of BeO

$$BeO + 2NH_4HF_2 \rightarrow (NH_4)_2BeF_4 + H_2O$$

  - Fluoride could be complexed with Pu, not allowing complete dissolution of BeO
    - A small amount of HF (0.05-0.1M HF/8-12M HNO_3) is desirable for PuO_2 dissolutions
  - Complicated optical spectra of actinides justified PuO_2 interference testing

Interference Testing

- **CeO_2 used in initial testing**
  - Ce is safer, cheaper, easier to obtain, and easier to dispose than Pu
    - Obtained from Aldrich, >99.9% metals basis, <5 micron powder
    - CeO_2 was utilized instead of Ce metal to minimize H_2 gas generation
    - Ce was used in cold runs at SRS before Pu processing Canyons were placed online
- **PuO_2 used to confirm CeO_2 testing**
  - NBL CRM No. 122 PuO_2 in powder form
    - Limited to 3 grams of CRM No. 122
    - <1 µg/g beryllium impurity
  - Concentrated Pu solutions were not considered due to low pH

New Brunswick Laboratory
Certified Reference Materials
Certificate of Analysis

CRM No. 122

Plutonium Oxide - PuO_2
In Powder Form
(Plutonium Assay and Isotopic Standard)

(In cooperation with the University of California
Los Alamos National Laboratory, Los Alamos, New Mexico)

Plutonium	87.790 ± 0.039 Wt.%* (877.90 ± 0.39 $g \cdot kg^{-1}$)
Plutonium-238	0.0521 ± 0.0011 At. %*
Plutonium-239	87.305 ± 0.004 At. %*
Plutonium-240	11.539 ± 0.004 At. %*
Plutonium-241	0.9248 ± 0.0011 At. %*
Plutonium-242	0.1790 ± 0.0013 At. %*
Relative Atomic Weight	239.191*

Interference Testing – Cerium Oxide

- **Performed with and without blank sampling media (GhostWipe™)**
- **3 wt% ABF solvent**
  - CeO_2 used as PuO_2 surrogate
- **CeO_2 material tested at:**
  - 0.1 gram CeO_2
  - 0.25 gram CeO_2
  - 0.5 gram CeO_2
- **Undissolved CeO_2 material was observed (pale yellow) following heat cycle**
- **ABF solution was colorless following heat cycle**

Sample ID	Instrument Result (ppb)	
	with blank wipe	without blank wipe
Prep Blank (PB)	0.03	
Indep. Cal. Verif. (ICV)		2.00
BeO 0.2 µg Be		0.47 (0.19 µg Be)
BeO 0.5 µg Be		1.33 (0.53 µg Be)
BeO 0.2 µg Be	0.43 (0.17 µg Be)	
BeO 0.5 µg Be	1.18 (0.47 µg Be)	
LCS 0.25 ppb Be, no Ce	0.24	0.27
LCSD 0.25 ppb Be, no Ce	0.26	0.42
LCS 0.5 ppb Be, no Ce	0.47	0.59
LCSD 0.5 ppb Be, no Ce	0.46	0.52
LCS 2.0 ppb Be, no Ce	1.78	2.04
LCSD 2.0 ppb Be, no Ce	1.78	2.11
LCS 0.25 ppb Be, 0.1g Ce	0.24	0.24
LCSD 0.25 ppb Be, 0.1g Ce	0.26	0.35
LCS 0.5 ppb Be, 0.25g Ce	0.45	0.53
LCSD 0.5 ppb Be, 0.25g Ce	0.45	0.53
LCS 2.0 ppb Be, 0.5g Ce	1.72	2.05
LCSD 2.0 ppb Be, 0.5g Ce	1.74	2.07

Interference Testing – Plutonium Oxide

- **Performed with and without blank sampling media (GhostWipe™)**
- **3 wt% ABF solvent**
  - PuO_2 powder used to confirm CeO_2 testing
- **PuO_2 CRM material tested at:**
  - 0.1 gram PuO_2
  - 0.25 gram PuO_2
  - 0.5 gram PuO_2
- **Undissolved PuO_2 material was observed (black) following heat cycle**
- **ABF solution was colorless following heat cycle**

Sample ID	Instrument Result (ppb)	
	with blank wipe	without blank wipe
Prep Blank (PB)	0.03	
Indep. Cal. Ver. (ICV)		1.99
BeO 0.2 µg Be	0.48 (0.19 µg Be)	
BeO 0.5 µg Be	1.30 (0.52 µg Be)	
0.5g Pu/no Be	0.03	0.04
0.25g Pu/no Be	0.05	0.04
0.25g Pu/no Be	0.03	0.02
0.1g Pu/no Be	0.11	0.04
0.1g Pu/no Be	0.03	0.02

Conclusion

- **Optical fluorescence method successfully setup in glovebox**
- **CeO_2 and PuO_2 interference testing confirmed no significant impact to beryllium measurements at tested levels**
- **Method utilized on "real" samples**
- **AIHA accredited Be results were reported to the customer**
- **Lower report limit = 0.1 µg Be/wipe**
  - 0.25 ppb at instrument
  - Total 400x dilution (20x extraction + 20x detection)
  - Additional testing necessary to obtain lower report limit

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Questions?